

II. "The Complexity and the Dissociation of the Molecules of Liquids." By Professor W. RAMSAY, Ph.D., F.R.S. Received April 26, 1894.

Since the publication of a research on the molecular complexity of liquids by Ramsay and Shields ('Trans. Chem. Soc.,' vol. 63, p. 1191) two questions have arisen:—First: What other evidence is there as to the existence of complex molecules in certain liquids?

Second: How can the amount of dissociation of associating liquids be inferred from measurements of their surface-energy?

The first of these questions has been treated of by Professor Philippe Guye, in the 'Archives des Sciences Physiques et Naturelles de Genève,' 31; and as that periodical is not easily accessible to English readers, a short account of his article is given here.

I. *Evidence in favour of the Molecular Complexity of Certain Liquids.*

a. Guye has shown ('Annales,' vol. 31, [6], p. 206) that the quotient obtained by dividing the absolute critical temperature of a liquid by the critical pressure measured in atmospheres is equal to the molecular refraction of the liquid multiplied by a factor which is approximately equal to 1.8. His reason for this statement is as follows:—Equations such as that of van der Waals, which express approximately the constants for gases and liquids in terms of temperature, pressure, and volume, assume as one of their data the "co-volume" (*b*) of the substance; *i.e.*, a number proportional to the actual volume of the molecules, supposing them to be spherical. The dielectric constant of a body *k*, according to Clausius, depends on the ratio *u* of the real volume to the apparent volume occupied by the molecules, in such a manner that

$$u = (k-1)/(k+2).$$

Maxwell has shown that according to the electro-magnetic theory of light, the dielectric constant *k* should be equal to the square of its index of refraction for a ray of light of infinite wave-length; hence

$$u = \frac{(n^2-1)}{(n^2+2)}.$$

The name molecular refraction is given to this quantity referred to the volume of 1 gram, and multiplied by the molecular weight, or

$$\frac{u}{d} M = \frac{(n^2-1)}{(n^2+2)} \cdot \frac{M}{d} = MR,$$

where MR signifies molecular refraction.

Now van der Waals has shown that the relations between critical temperature, pressure, and volume are given by the equation

$$\frac{3}{8}(1+\alpha\theta) = \frac{\pi\phi}{(1+3\pi\phi^2)(1-\phi/3)}.$$

The denominator on the right-hand side of the equation is nearly equal to unity. Assuming this to be the case, and introducing the value of  $\alpha = \frac{1}{273}$ ,

$$k = \frac{273+\theta}{\pi} = \frac{8}{3} \cdot 273\phi,$$

where  $k$  is the "critical coefficient," or the critical temperature divided by the critical pressure.

Now the value of  $\phi$  is related to  $b$  by the equation

$$\phi = 3b,$$

and  $b$  being proportional to the molecular refraction, the relation

$$k = \frac{273+\theta}{\pi} = \frac{1}{f} \cdot \frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \frac{1}{f} MR$$

should hold. That is,  $k$ , the quotient obtained on dividing the absolute critical temperature by the critical pressure, should, when multiplied by a constant, be equal to the molecular refraction.

While the majority of substances examined by Guye appear to consist of simple molecular groups at their critical points, water, methyl alcohol, and acetic acid yield numbers which point to association, inasmuch as the constant  $f$ , instead of having its usual value 1.8, has decreased to about 1.1.

*b.* The densities of most liquids at their critical points may be found by multiplying their theoretical densities by a number approximately equal to 3.85 (Young and Thomas, 'Trans. Chem. Soc.,' 1893, p. 1251; also 'Phil. Mag.,' 1892, p. 507). But for a few substances the following values were found:—

Methyl alcohol.....	4.52
Ethyl alcohol.....	4.02
Propyl alcohol.....	4.02
Acetic acid .....	5.00

The factor should be greater, if association occurs, because the theoretical density calculated by Boyle's and Gay-Lussac's laws would then be greater than if it were supposed that the molecules of methyl alcohol, for example, were represented by the simple formula  $\text{CH}_4\text{O}$ . Here, again, the evidence points to complex molecules at the critical temperature.

c. Cailletet and Matthias have suggested a simple plan for finding the true volume of a substance at its critical point. It consists in mapping the densities in the state of liquid and of gas against temperature (as seen, for example, in the diagram given by Ramsay and Young in their memoir on alcohol in the 'Philosophical Transactions,' 1886, Part I, plate 7), and bisecting the lines of equal pressure, which cross the diagram horizontally. Such lines are lines of equal pressure at constant temperature. On joining the points where the lines are bisected, a straight line is obtained in the case of most liquids, which, when continued vertically, cuts the curve at the critical density. But to this rule Young and Thomas find that water, and methyl, ethyl, and propyl alcohols are exceptions, for they give curved lines. These substances are not associated in the state of gas, although in the liquid state they display association. Acetic acid, however, which displays association both in the state of liquid and of gas, gives a line which is, if not quite, at least very nearly straight.

It may therefore be concluded that while a curved line implies association in the state of liquid, a straight line implies either no association or association in both conditions.

d. The heat required to vaporise a dissociating liquid is employed in two ways when the gas, as is always the case, has a simpler molecular formula than the liquid. A portion of the heat is employed in vaporisation alone; while a portion is absorbed in effecting the decomposition of complex molecular groups. The heat of vaporisation alone diminishes as temperature rises, till at the critical point it is zero; but the heat required to dissociate molecular groups may increase, if that term is of importance, and may cause the total heat to increase. The researches of Ramsay and Young on ethyl alcohol and on acetic acid have shown that there exist maxima in the heats of vaporisation of these substances. Thus at 0°, the heat of vaporisation of ethyl alcohol is 220.9 cal.; at 10°, 221.2; at 20°, 220.6; and at 30°, 220.1. The numbers then decrease as usual. With acetic acid at 80°, the value is 91.6 cal.; at 100°, 92.3; at 110°, 92.8; at 120°, 92.7; at 130°, 92.4, and so on. It may be stated, then, that when the numbers representing heats of vaporisation of a compound increase to a maximum, and then diminish, the compound contains complex molecules in the liquid state. It does not follow that all substances which possess complex liquid molecules must exhibit such a maximum, for this peculiarity evidently depends on the relative importance of the heats of dissociation and of vaporisation.

e. The curves representing the vapour pressures of non-dissociating liquids do not cut one another at any point in their course. Liquids which associate give vapour-pressure curves which cut some of those

of non-dissociating liquids and frequently cut those of dissociating liquids. The fact, then, that the vapour-pressure curve of a liquid cuts those of undeniably simple substances, such as benzene, carbon tetrachloride, &c., may be taken as a proof that that liquid contains complex molecules.

*f.* This relation may also be expressed by the factor in van der Waals' equation for calculating vapour-pressures, viz. :—

$$\log pc - \log p = f \frac{T_c - T}{T},$$

where *pc* is the critical pressure; *T<sub>c</sub>* the critical temperature; and *p* some other pressure at temperature *T*. The constant *f* has a value close to 3 for all non-associating compounds. Thus from Young's results the following values of *f* are calculated :—

	<i>f.</i>		<i>f.</i>
Benzene.....	2.89	Propyl formate ....	3.04
Chlorobenzene .....	2.95	Methyl acetate ....	3.07
Fluorobenzene .....	2.99	Ethyl acetate.....	3.26
Carbon tetrachloride	2.81	Propyl acetate ....	3.22
Tin tetrachloride ....	3.01	Methyl propionate..	3.13
Ethyl oxide.....	3.00	Ethyl propionate ..	3.22
Methyl formate .....	3.00	Methyl butyrate....	3.25
Ethyl formate .....	2.97	Methyl isobutyrate..	3.15

The mean value is 3.06.

But for liquids with complex molecular groupings the values are considerably higher, and, moreover, are not constant.

	<i>f.</i>
Methyl alcohol.....	3.56 to 3.77
Ethyl alcohol .....	3.58 „ 4.02
Propyl alcohol .....	3.49 „ 3.77
Acetic acid .....	3.36 „ 3.49
Water .....	3.20 „ 3.24

Other relations besides those mentioned by Guye, of whose memoir the preceding pages give an abstract, also point towards the molecular complexity of the alcohols and acids. Among them may be mentioned the ratios of the volumes of saturated vapour at some chosen pressure to that at the critical pressure, as shown in p. 1257 of Young's memoir (*loc. cit.*); the greater values of the expression  $(dp/dt)T$  for the alcohols and for water compared with those of other substances (see Ramsay and Young, 'Proc. Phys. Soc.,' VII, p. 303); this really means the greater heat of vaporisation for unit increase of volume, for  $(dp/dt)T$  is equivalent to  $L/(S_1 - S_2)$ . This

fact indeed is pointed out in the first part of the series of papers (*ibid.*, 291). Again the ratios of total to external work produced on evaporation (*ibid.*, 293) show that the total work is a higher multiple of the external work or work employed in expansion against pressure, in the case of the alcohols, acetic acid, and water, than in the case of other compounds.

Enough has been said to show that a great mass of evidence exists in favour of molecular complexes in certain liquids. It remains now to consider the methods by which the degree of complexity can be ascertained.

## II. Methods of Deducing the Molecular Complexity of Liquids from Measurements of their Molecular Surface-energy.

It was shown by Ramsay and Shields ('Phil. Trans.,' 1893, A, 662) that the relation of molecular surface-energy of many liquids to temperature may be expressed by the equation

$$(1) \quad \gamma (Mv)^{\frac{2}{3}} = k(\tau - d),$$

where  $\gamma$  is surface-tension, measured in dynes,  $(Mv)^{\frac{2}{3}}$  the molecular surface measured in square centimetres,  $k$  is an approximate constant for most liquids varying little from 2.12, and  $\tau$  is the temperature numbered downwards from the critical point;  $d$  is a nearly constant number of degrees, usually  $5^{\circ}$ , which must be subtracted from  $\tau$ .

For liquids which associate, such as the alcohols and fatty acids, the value of  $k$  is not constant, but increases with rise of temperature.

The problem is, knowing the average value of  $k$  for non-associating liquids, to deduce the average molecular weights of associating liquids at any given temperature.

Differentiating equation (1) we obtain

$$\frac{d}{dt} \cdot \gamma (Mv)^{\frac{2}{3}} = k,$$

for non-associating liquids; or, if we insert a term  $x$ , to represent a factor with which the gaseous or normal molecular weight of a liquid should be multiplied in order that the normal value of  $k$  should result from the equation, we obtain

$$(2) \quad \frac{d}{dt} \cdot \gamma (xMv)^{\frac{2}{3}} = k,$$

In our first attempts to deduce the true average value of  $M$  for associating liquids, equation (2) was expanded, thus:—

$$(3) \quad x^{\frac{2}{3}} \cdot \frac{d}{dt} \gamma (Mv)^{\frac{2}{3}} + \gamma (Mv)^{\frac{2}{3}} \cdot \frac{dx^{\frac{2}{3}}}{dt} = k;$$

and it was assumed, as a first approximation, that the second term, the variation of  $x^{\frac{2}{3}}$  with temperature, was negligible. In such a case

$$(4) \quad x = \left\{ k \frac{dt}{d\gamma (Mv)^{\frac{2}{3}}} \right\}^{\frac{3}{2}};$$

and it was on this assumption that the results given in the papers referred to for the alcohols, the acids, and water were calculated.

The numbers obtained were, however, as will be shown, much in excess of the truth.

An attempt was made to approximate to the true value of  $x$ , by calculating it by means of equation (4) approximately, and using the results obtained to correct equation (3), by inserting the neglected second term. This was found to be impossible, and to lead to absurd results; hence it was inferred that the variation of  $x$  with temperature was such as to make it imperative that attention should be paid to the second term of equation (3). At the same time it was noticed in mapping  $x$  that its alteration with temperature was approximately linear; and this fact greatly simplified the problem.

Mr. J. Rose-Innes, who has taken much interest in this work, and has on several occasions given valuable assistance, was kind enough to endeavour to find an expression which would satisfy these conditions.

A formula of the form

$$(5) \quad \gamma M v^{\frac{2}{3}} = \frac{k(\tau - d)}{1 + \mu \tau}$$

agrees admirably with the experimental values of molecular surface-energy for methyl and ethyl alcohols, water, and acetic acid between low temperatures and some  $30^{\circ}$  below their critical points. Even at  $-89.8^{\circ}$ , it will be noticed, the agreement for methyl and ethyl alcohols is reasonably good.

The constants for these substances are:—

	$k$ .	$d$ .	$\mu$ .	Critical temperature.
Methyl alcohol.....	1.489	—4.22	0.00104	240.0°
Ethyl alcohol.....	2.170	4.8	0.00193	243.1
Water.....	2.631	19.5	0.00218	358.1
Acetic acid.....	1.910	11.9	0.00163	321.5

A comparison between the calculated and found values of  $\gamma(Mv)^{\frac{2}{3}}$  is given in the following table:—

Methyl alcohol.				Ethyl alcohol.				Water.				Acetic acid.			
T.	$\tau$ .	$\gamma(Mv)^{\frac{1}{3}}$ .		T.	$\tau$ .	$\gamma(Mv)^{\frac{1}{3}}$ .		T.	$\tau$ .	$\gamma(Mv)^{\frac{1}{3}}$ .		T.	$\tau$ .	$\gamma(Mv)^{\frac{1}{3}}$ .	
		Found.	Calcd.			Found.	Calcd.			Found.	Calcd.			Found.	Calcd.
-89.8	329.8	361.8	369.8	-89.8	332.9	436.1	433.3	0	368.1	502.9	503.5	20	301.5	371.2	371.1
+20	290	271.4	271.4	+20	223.1	331.0	331.0	20	338.1	485.3	484.9	40	281.5	..	353.2
70	170	216.2	220.4	40	203.1	307.3	309.0	40	318.1	466.3	466.3	60	261.5	..	334.4
90	150	196.3	198.6	60	183.1	284.8	285.8	60	298.1	446.2	446.4	80	241.5	..	314.8
110	130	176.7	176.0	80	163.1	261.2	261.1	80	278.1	425.3	425.5	100	221.5	..	294.3
130	110	154.8	152.5	100	143.1	235.0	235.1	100	258.1	403.5	403.5	120	201.5	..	272.7
150	90	131.3	128.3	120	123.1	208.0	207.3	120	238.1	380.7	380.3	140	181.5	250.2	250.0
170	70	104.8	103.0	140	103.1	178.8	177.8	140	218.1	357.0	355.6	160	161.5	226.3	226.1
180	60	91.0	90.0	160	83.1	147.2	146.4					180	141.5	200.2	201.2
190	50	76.1	76.8	180	63.1	112.6	112.7					200	121.5	174.9	174.7
200	40	60.6	63.2	200	43.1	75.7	76.7					220	101.5	146.9	146.9
210	30	45.4	49.4	210	33.1	57.1	57.7					240	81.5	117.5	117.3
220	20	29.2	35.3	220	23.1	39.2	38.0					260	61.5	86.0	86.1
				230	13.1	19.8	17.6					280	41.5	54.8	52.9

It may be remarked that at temperatures within 20 or 30 degrees of the critical point the former no longer accurately expresses the results. This is not peculiar to associating compounds, as has already been shown in the 'Phil. Trans.,' *loc. cit.*, p. 657. Should it be desired to secure more accurate correspondence between the found data near the critical temperatures and those calculated, the last term may be modified. The equation then becomes

$$\gamma(Mv)^{\frac{2}{3}} = \frac{k\tau - kd(1 - 10^{-\lambda\tau})}{1 + \mu\tau}.$$

For ethyl alcohol, the value of  $\lambda$  is 0.044, and, on introducing this correction, the calculated values near the critical point, above 180°, are as follow :—

T.	$\tau$ .	$\gamma Mv^{\frac{2}{3}}$ .		T.	$\tau$ .	$\gamma Mv^{\frac{2}{3}}$ .	
		Found.	Calctd.			Found.	Calctd.
°	°						
240	3.1	3.7	3.9	200	43.1	75.7	76.9
236	7.1	9.9	9.9	190	53.1	94.9	95.1
234	9.1	13.3	13.2	180	63.1	112.6	112.8
230	13.1	19.8	20.3	178	73.1	130.1	129.9
220	23.1	39.2	39.0	160	83.1	147.2	146.4
210	33.1	57.1	58.1	150	93.1	163.0	162.5

Similar corrections could be introduced for methyl alcohol, acetic acid, and water, which would have the effect of reproducing the experimental numbers at low values of  $\tau$ .

The following considerations show how it is possible to calculate the degree of association of such compounds at any desired temperature. Neglecting for the present the " $\lambda$ " term, which is introduced to secure concordance at temperatures near the critical point, let us consider equation (1), where  $k$  has the value 2.121 for unassociating liquids, viz.,

$$\gamma(Mv)^{\frac{2}{3}} = 2.121 (\tau - d).$$

Supposing that the liquid is composed partly of complex molecules, and that  $x$  is a measure of the complexity, we should have

$$\gamma(xMv)^{\frac{2}{3}} = 2.121 (\tau - d),$$

or

$$\gamma(Mv)^{\frac{2}{3}} = 2.121 \times \frac{1}{x^{\frac{2}{3}}} \times (\tau - d).$$



Comparing this with equation (5), which reproduces the results for associating liquids with fair accuracy,

$$\gamma (Mv)^{\frac{2}{3}} = k (\tau - d) / (1 + \mu\tau),$$

it is evident that  $x$  corresponds to the expression

$$\left\{ \frac{2 \cdot 121}{k} (1 + \mu\tau) \right\}^{\frac{3}{2}}.$$

It is, of course, easy to include the " $\lambda$ " term, when  $x$  follows, as before.

There can, I think, be no doubt that this method gives a correct value to the factor of association, within certain limits. These limits are conditioned by the fact that the number chosen for  $k$ , viz., 2·121, is not absolutely constant, but varies with the nature of the compound. The extreme variation found for the fourteen substances which have been most carefully investigated is between 2·020 for ethyl formate, and 2·248 for methyl isobutyrate. On the assumption that this is the extreme divergence, there may be an error of 5 per cent. in a negative or positive direction caused by assuming the mean value 2·121.

But there is another assumption involved in such calculations. It is that a mixture of two liquids possesses such a molecular surface-energy that the mean molecular weight of the mixture, calculated from the proportion in which they are present in the mixture, shall be deducible from the molecular surface-energy. It is conceivable that the surface of such a mixture should not exhibit the same distribution of molecules as the interior, and evidence is required to show that the assumption that it does is correct. This evidence is given in another communication, and it appears therefore that the assumption is justified.

With these premises, therefore, I proceed to give the molecular association of methyl and ethyl alcohols, water, and acetic acid.

Methyl alcohol.				Ethyl alcohol.			Water.			Acetic acid.		
T.	$\tau$ .	$\alpha$ .		T.	$\tau$ .	$\alpha$ .	T.	$\tau$ .	$\alpha$ .	T.	$\tau$ .	$\alpha$ .
- 89° 8'	329° 8'	2° 65	- 89° 8'		332° 9'	2° 03	0°	358° 1'	1° 707	20°	301° 5'	2° 13
+ 20	220	2° 32	+ 20		223° 1	1° 65	20	338° 1	1° 644	40	281° 5	2° 06
70	170	2° 17	40		203° 1	1° 59	40	318° 1	1° 582	60	261° 5	1° 99
90	150	2° 11	60		183° 1	1° 52	60	298° 1	1° 523	80	241° 5	1° 92
110	130	2° 06	80		163° 1	1° 46	80	278° 1	1° 463	100	221° 5	1° 86
130	110	2° 00	100		143° 1	1° 39	100	258° 1	1° 405	120	201° 5	1° 79
150	90	1° 94	120		123° 1	1° 33	120	238° 1	1° 346	140	181° 5	1° 72
170	70	1° 89	140		103° 1	1° 27	140	218° 1	1° 289	160	161° 5	1° 66
180	60	1° 86	160		83° 1	1° 21	..	..	..	180	141° 5	1° 59
190	50	1° 83	180		63° 1	1° 15	..	..	..	200	121° 5	1° 53
200	40	1° 81	200		43° 1	1° 09	..	..	..	220	101° 5	1° 47
210	30	1° 78	210		33° 1	1° 06	..	..	..	240	81° 5	1° 41
220	20	1° 75	220		23° 1	1° 03	..	..	..	260	61° 5	1° 35
			230		13° 1	1° 00	..	..	..	280	41° 5	1° 30

## Addendum.

Since the foregoing pages were written, Professor van der Waals has published a long memoir on the "Thermodynamic Theory of Capillarity on the Assumption of Continuous Change of Density" ('*Zeitschrift für physikalische Chemie*,' vol. 13, pp. 657—725). On the main part of his work I have no criticism to offer; but on p. 714, he states some objections to the method previously employed by Ramsay and Shields in calculating the factor of association  $\alpha$ . These remarks are fully justified, as will have been seen from the preceding pages of this paper; but in the formula which he suggests to replace it, he makes an assumption which, at first sight, is no less untenable than our assumption that the factor of association,  $\alpha$ , does not vary with temperature. In placing the factor of association as equal to unity at temperatures near the critical temperature, he obtains the formula

$$\alpha^3 = \frac{k(\tau' - \tau) + \gamma(Mv)^{\frac{2}{3}}}{\gamma(Mv)^{\frac{2}{3}}},$$

and, inasmuch as this assumption is apparently very nearly true for methyl and ethyl alcohols and for acetic acid, the numbers he gives are nearly identical with those in the last table of this paper. But they differ in the case of water, and  $\alpha$ , according to him, is equal to 1.9, instead of to 1.707.

The formula given by him on p. 716 to calculate  $\gamma$  yields remarkably good results. In fact, if  $\gamma$  be calculated for ether at  $-89.8^\circ$ , a result is obtained identical with that found. This result was unforeseen by van der Waals, for the value for  $\gamma$ , 30.65, was not given by us at that low temperature in our previous paper.

Professor van der Waals, however, makes two criticisms which appear to me to be hardly justified. The first refers to a correction applied by us in order to allow for the capillarity in the wider, yet still narrow, tube in which the capillary tube stood. He thinks that this correction would be affected by the curvature of the meniscus not being the same at high as at low temperatures. The remark is certainly true; but as the alteration in height due to altered curvature of meniscus would be well within the range of experimental error, it is negligible. The second criticism deals with the capillarity near the critical point, and van der Waals states that the simple formula, applicable to narrow tubes, no longer holds when the capillary rise is only a few times greater than the radius of the tube. This objection would be justified were it not that the capillary heights are nearly a linear function of the temperature; and with non-dissociating liquids, which he is here considering,

it is quite unnecessary to take measurements at temperatures very close to the critical temperature, because, if that temperature is known, there can be only one curve joining the points experimentally found at somewhat lower temperatures and the critical temperature. The form of the curve is such that no doubt can exist as to its course. Indeed, with chlorobenzene, measurements were not carried out at all in the immediate neighbourhood of the critical point, but only at much lower temperatures, and yet there could be no question as to the course of the curve, when it was mapped. But these are minor points; and it is very gratifying to find that the material provided by Dr. Shields and myself affords such a remarkable confirmation of the justice of Professor van der Waals' views.—18th May, 1894.

III. "The Molecular Surface-Energy of Mixtures of non-associating Liquids." By Professor WILLIAM RAMSAY, Ph.D., F.R.S., and Miss EMILY ASTON, B.Sc. Received April 26, 1894.

It has been shown in the previous paper that it is possible to calculate the degree of association of an associating liquid such as alcohol, on the assumption that molecules of less complexity remain uniformly distributed along with molecules of greater complexity throughout the liquid, and that no one kind of molecule tends to congregate on the surface to the exclusion of the other. It is necessary, however, to justify this assumption; and for this reason experiments have been made on mixtures of liquids the molecules of which do not unite to form complex groups; such are most of the liquids investigated by Ramsay and Shields ('Trans. Chem. Soc.,' vol. 63, p. 1099, *et seq.*).

The experiments of which an account is here given, show that while the height to which a mixture of two liquids ascends in a capillary tube is not the mean of the heights to which each singly would ascend at the same temperature, while the surface-tensions and the surface-energies are not necessarily the mean of those possessed by the liquids unmixed with each other, regard being paid to their relative proportion in the mixture, yet the coefficient of decrease of molecular surface-energy, and consequently the calculated molecular weights, are true means of those of the two liquids.

The substances used in these experiments were chosen in pairs, and as it was necessary in closing the tubes to evaporate some of the contained liquid in order to ensure the expulsion of air, mixtures of such liquids were taken as possess approximately equal boiling points, so